at 942 cm^{-1} to 3% to 958 cm^{-1} for large conversions. Additional product selectivity in the *trans*-butene reaction may be possible by altering the laser fluence and pressure of *trans*-butene, along with the laser frequency and the number of laser pulses. In focused beam experiments, it is difficult to predict the effects of changing the fluence and pressure.[17,18] However, in collimated beam experiments, both fluence and pressure affect the branching ratio in two channel reactions.[16,18] In a previous study of *trans*-butene utilizing a collimated beam, about 20% decomposition occurred with the isomerization reaction at 4.5 J/cm^2. At fluences above 6 J/cm^2, fragmentation was found to dominate isomerization.[10] Hence, a greater control over the product distribution from the multiphoton reaction of *trans*-2-butene may be achieved by altering the fluence and gas pressure, together with the laser frequency.

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Registry No. *trans*-2-Butene, 624-64-6; *cis*-2-butene, 590-18-1; ethylene, 74-85-1; ethane, 74-84-0; propylene, 115-07-1; propyne, 74-99-7; 1,3-butadiene, 106-99-0; 1-butadiene, 106-98-9; 2-butyne, 503-17-3.

Infrared Multiphoton Decomposition of *cis*-2-Pentene and 3-Methyl-*cis*-2-pentene[†]

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The infrared multiphoton (IRMP) decomposition of *cis*-2-pentene and 3-methyl-*cis*-2-pentene has been studied in order to compare the fragmentation pattern of the photoexcited molecules with that observed in the vacuum ultraviolet photolysis. The decompositions were studied at pressures from 0.2 to 5 Torr, using a pulsed CO$_2$ laser weakly focused to give fluences from about 5 to 20 J/cm^2 in the focal region. The IRMP decomposition of both molecules can be explained on the basis of a primary dissociation of a β C–C bond, followed by secondary fragmentation of the allylic moiety and the usual stabilizing processes and radical–radical reactions. The fragmentation patterns are generally similar to those observed in the vacuum UV photolysis, and the present results simply show the possibility that the ground state is involved in the vacuum UV photolysis; the behavior of the latter system itself lends support to this. Differences between the two systems can be explained by the higher initial energy of the molecules excited in the vacuum UV. Some isomerization was also observed, mostly arising from radical–radical reactions. The formation of 1-pentene, however, indicates that the sigmatropic 1,3 hydrogen atom transfer can take place via the vibrationally excited ground state of *cis*-2-pentene. Conversely, 2-methyl-1-butene is not observed; its formation requires an internal methylene shift, and its occurrence in the vacuum UV photolysis suggests its direct formation from an electronically excited state.

Introduction

The photochemistry of gaseous alkenes excited directly in the vacuum ultraviolet is now well-known. The main observed feature is the fragmentation of the photoexcited molecule through the break of a C–C bond located in a position β to the double bond.[1-6]

From the pressure dependence of the quantum yields, it is generally accepted that the decomposing molecule is in its vibrationally excited ground state,[7] implying that the singlet excited state formed by the initial absorption has crossed back to the ground state. Moreover, when the alkenes are irradiated at wavelengths close to their absorption thresholds, isomerization as well as fragmentation occurs with significant quantum yields. The mechanisms leading to such isomerization are not completely clear; do they proceed directly from the electronically excited singlet states initially formed, or do they also involve the "hot" ground state?[8-11] Since the V(π–π^*) state has a skewed structure, it has the possibility of returning to the ground state in either the cis or trans configuration. It has also been proposed that the observed methylene shift, e.g., the formation of 2-methyl-1-butene in the photochemistry of *cis*-2-butene, involves the formation of a carbene intermediate from a Rydberg (Π-R(3s)) excited state.[12] Finally, there is some controversy about the nature of the excited state involved in the sigmatropic 1,3-hydrogen shift leading to the formation of 1-pentene in the *cis*-2-pentene photolysis.[10]

By using a pulsed infrared laser, it is possible through multiphoton absorption to increase the vibrational energy content of ground-state alkene molecules until they can decompose or isomerize.[13,14] Then, comparison with the vacuum UV photochemistry would be valuable, because in the infrared multiphoton (IRMP) decomposition or isomerization one may assume that only the "hot" ground state is involved. We have chosen *cis*-2-pentene for this study since its behavior in the vacuum UV region is well-known.[4-12] Moreover, its infrared absorption spectrum shows a strong band at one of the more intense lines of the CO$_2$ laser. We have also included here a few results obtained on the IRMP decomposition of 3-methyl-*cis*-2-pentene.

Experimental Section

A conventional TEA-203 Lumonics CO$_2$ laser, previously described,[15] was used as the radiation source. The N$_2$–CO$_2$–He gas mixture gave a pulse consisting of a sharp spike ($\simeq$50 ns) followed by a tail that extended for about 1 μs. The beam was stopped down to give a diameter of about 12 mm, which was maintained

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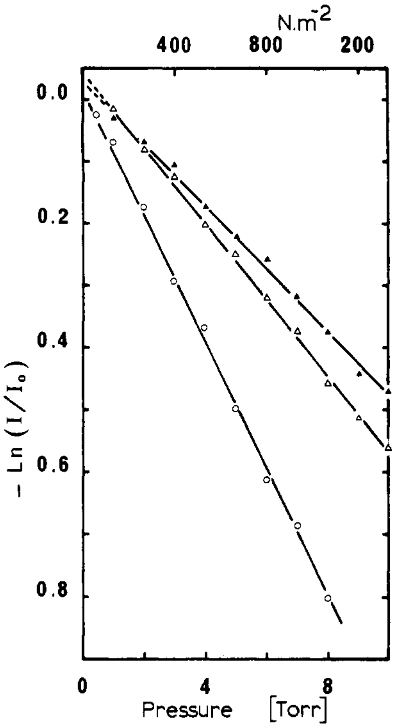

Figure 1. Decrease of the transmitted beam energy, *I*, with pressure of *cis*-2-pentene at 931.0 cm^{-1} and a central fluence of 8.4 J/cm^2 (○) and of 3-methyl-*cis*-2-pentene at 1052.3 cm^{-1} and central fluence of 7.3 J/cm^2 (△) and 0.15 J/cm^2 (▲).

at as uniform an intensity as possible. A lens with focal length of 50 cm was placed close to the front window of the reaction cell to give a weak focus at the center of the cell, which was 100 cm long and 25 mm in diameter, made of Pyrex with NaCl windows attached with O-ring seals. Fluence was reduced in some experiments by inserting a Ge plate in the laser beam in front of the lens. Pulse energy was measured by a Scientec 362 power meter just outside the exit window of the cell, where the beam had diverged again to about 15-mm diameter.

A conventional grease-free Pyrex vacuum line, with metal valves and an oil diffusion pump, was used to handle the gases. Pressure was measured with a Baratron capacitance manometer with a range of 0.001–12 Torr.

Alkenes were obtained commercially from API, degassed at −196 °C, and used without further purification. The *cis*-2-pentene had a stated impurity of 0.07% and contained about 25 ppm 1-pentene. The 3-methyl-*cis*-2-pentene had a stated impurity of 0.03% and contained less than 0.02% 2-ethyl-1-butene and 73 ppm 3,3-dimethyl-1-butene. Oxygen used was Matheson research grade. Gas chromatographic analysis was done with a flame ionization detector and a squalane column; an 8-m 5% tricresyl phosphate column in series with a 15-cm VZ-7 column (Alltech) was used to verify identification made on the squalane column and to separate 1-butene from 1,3-butadiene. In all experiments, the number of pulses was chosen so as to keep the consumption of the starting alkene to less than 0.25%.

Results

Absorption Measurements. The absorption of laser radiation by the two alkenes is shown in Figure 1. Except for some initial curvature (perhaps due to pressure-dependent absorption at low pressure), Beer's law is followed by both compounds. These measurements were made with the laser beam weakly focused as in the decomposition experiments and are based simply on measurement of the energy transmitted by the reaction cell as a function of alkene pressure. They correspond therefore to absorption both at high fluence in the central cylindrical focal zone (about 10 cm long) and at lower fluence in the converging and diverging beam at either end.

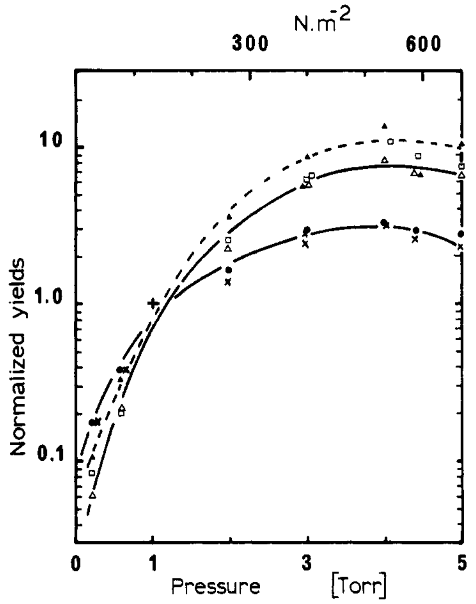

Figure 2. Pressure dependence of product formation in the *cis*-2-pentene decomposition. Yield per pulse for each product is normalized to that at a pressure of 1 Torr: (●) ethane; (△) propene; (□) 1,3-butadiene; (×) 3-methyl-1-butene; (▲) propane.

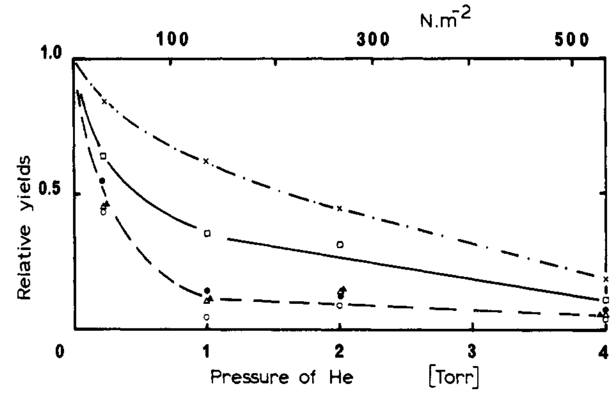

Figure 3. Effect of helium on the IRMP decomposition of 2 Torr of *cis*-2-pentene. Product yields relative to those in pure pentene: (●) ethane; (△) propene; (▲) propane; (□) 1,3-butadiene + 1-butene (75/25); (×) 3-methyl-1-butene.

Decomposition Measurements. No decomposition was observed in the unfocused beam, reflecting the rather weak absorption evident in Figure 1. Table I shows the quantities of products formed per pulse from *cis*-2-pentene with the focused beam under various conditions. The main products are ethane, 3-methyl-1-butene, 1,3-butadiene, 1-butene, propene, propane, and ethylene. Smaller quantities of methane, 2-butenes, and *n*-butane were also observed. There is a general increase in product yields with increasing pressure, which then level out and perhaps decrease at the highest pressure (5 Torr), shown in the normalized plots in Figure 2. The addition of 10% O_2 to *cis*-2-pentene markedly reduces the yields of products, varying with the nature of the product (Table I). The fluence also has a strong effect on product yields, with a reduction in fluence by a factor of 1.7 decreasing the ethane yields by a factor of 5–25 depending on pressure. Within the considerable experimental scatter, which was probably due largely to variations in fluence, there appears to be no systematic dependence of product yields on percentage conversion or number of pulses. The addition of helium to *cis*-2-pentene has a strong negative effect on the product yields (Figure 3). It is interesting to note that this effect was less in the case of 3-methyl-1-butene formation, larger (and similar) for 1,3-butadiene, 2-butene, and 1-butene, and even greater for the formation of propene, propane, and ethylene.

The main products formed in the IRMP decomposition of 3-methyl-*cis*-2-pentene are 2-methyl-1,3-butadiene (155), ethane (70), 2-methyl-1-butene (42), 2,3- and 3,3-dimethyl-1-butene (32), and ethylene (8); the numbers in brackets are yields per pulse in

TABLE I: Product Yields in the IRMP Decomposition of *cis*-2-Pentene

				product yield, pmol/pulse									
expt	p, torr	fluence, J/cm^2	no. pulses	CH$_4$	C$_2$H$_4$	C$_2$H$_6$	C$_3$H$_6$	C$_3$H$_8$	1-C$_4$H$_8$	C$_4$H$_6$	C$_4$H$_{10}$	2-C$_4$H$_8$	(CH$_3$)$_2$CHCH=CH$_2$
27	1.00	14	40			15.0	2.38	0.85	3.1	9.4			21.5
29	1.00	14	700	0.69	1.68	29.6	4.76	2.89	6.3	18.8	0.11	0.56	17.7
30	4.00	14	700	5.8	8.85	49.1	19.3	11.5	32.3	97.1			37.6
31	0.20	14	140		0.14	2.62	0.14	0.09	0.26	0.77			2.12
32	1.97	14	420	0.66	1.07	24.0	5.1	3.0	7.8	23.5			16.5
33	0.60	14	420	0.065	0.20	5.8	0.5	0.28	0.6	1.9			4.42
34	5.00	14	560	4.9	7.75	42.1	15.5	8.8	23.2	69.6		4.66	27.2
35	3.00	14	560	3.46	5.8	48.9	13.5	7.6	19.1	57.6	0.35	2.56	28.5
46	3.00	14	868	1.46	2.97	27.6	7.72	4.5	10.9	37.3			20.7
47	1.00	14	1160	0.78	0.44	9.47	1.37	0.83	1.9	5.6			7.45
48	4.40	14	840	1.41	4.48	27.4	9.30	5.46	13.0	49.0			18.8
52	4.00	19	952	<0.4	2.2	5.0	2.7	0.44	6.0	18.0		0.9	6.1
53	2.00	19	952	<0.3	2.02	4.5	3.6	0.21	3.0	8.7		0.35	3.4
54	2.00	19	952	6.54	4.8	41.8	11.2	6.85	16.9	55.0	0.35	2.26	28.8
37	4.96	8.4	840		0.15	2.35	0.47	0.17	0.57	1.68			1.69
38	1.00	8.4	1568		0.11	1.89	0.22	0.09	0.22	0.66			1.09
39	2.92	8.4	1680		0.11	1.62	0.24	0.09	0.30	0.93			1.20
40	0.60	8.4	1680		0.08	1.02	0.12	0.04	0.11	0.33			0.52
41	0.20	8.4	1680			0.5	0.07	0.02	0.05	0.14			0.20
43	4.00	8.4	2520		0.12	1.35	0.29	0.11	0.36	1.09			0.95
45	2.00	8.4	1680		0.06	0.93	0.12	*b*	0.14	0.42			0.66

[a] 10% O$_i$ added. [b] not measured.

picomoles for a typical experiment at 4 Torr and a fluence of about 18 J/cm^2 in the central cylinder of the focused beam. A strong dependence on fluence was again observed, and added oxygen sharply reduced product yields.

Isomerization. With regard to the several possible isomerizations of *cis*-2-pentene, we have not observed formation of 2-methyl-1-butene, but small amounts of 1-pentene were formed; because of a small impurity of this isomer in the starting material, the error in measuring its yield was rather large (Figure 4). The dependence of the yield of 1-pentene on pressure and added helium followed roughly those of the other products. The cis–trans isomerization of *cis*-2-pentene was not studied, but this process has already been observed in other laboratories.[13,14]

With regard to isomerization of 3-methyl-*cis*-2-pentene, interference by products of radical–radical reactions and a high level of isomeric impurities in the starting material precluded any firm conclusions. A surprising observation was the formation in the presence of oxygen of relatively large yields of 2-ethyl-1-butene and 3-methyl-*trans*-2-pentene, both isomers of the starting material, which were not observed from the pure alkene.

Discussion

Reactions of cis-2-Pentene. The products of the decomposition of *cis*-2-pentene reported in Table I are very similar to those observed in the vacuum UV photolysis. They may be rationalized on the basis of a mechanism involving the primary split of a β C–C bond, the weakest bond in the molecule, a mechanism very similar to that proposed for the vacuum UV photolysis,[4,12] followed by simple reactions of free radicals,

$$cis\text{-}2\text{-}C_5H_{10} \overset{nh\nu,\ M}{\rightleftharpoons} cis\text{-}2\text{-}C_5H_{10}^{\ddagger} \qquad (1)$$

$$cis\text{-}2\text{-}C_5H_{10}^{\ddagger} \rightarrow CH_3 + CH_3CHCHCH_2 \qquad (2)$$

$$\Delta H = +300 \text{ kJ mol}^{-1}$$

$$CH_3CHCHCH_2 \rightarrow H + 1{,}3\text{-}C_4H_6 \qquad (3)$$

$$\Delta H = +205 \text{ kJ mol}^{-1}$$

$$2CH_3 \rightarrow C_2H_6 \qquad (4)$$

$$CH_3 + CH_3CHCHCH_2 \rightarrow CH_4 + 1{,}3\text{-}C_4H_6 \qquad (5a)$$

$$\rightarrow CH_2{=}CHCH(CH_3)_2 \qquad (5b)$$

$$\rightarrow 2\text{-}C_5H_{10} \qquad (5c)$$

$$2CH_3CHCHCH_2 \rightarrow 1{,}3\text{-}C_4H_6 + C_4H_8 \qquad (6a)$$

$$\rightarrow C_8 \text{ dimers} \qquad (6b)$$

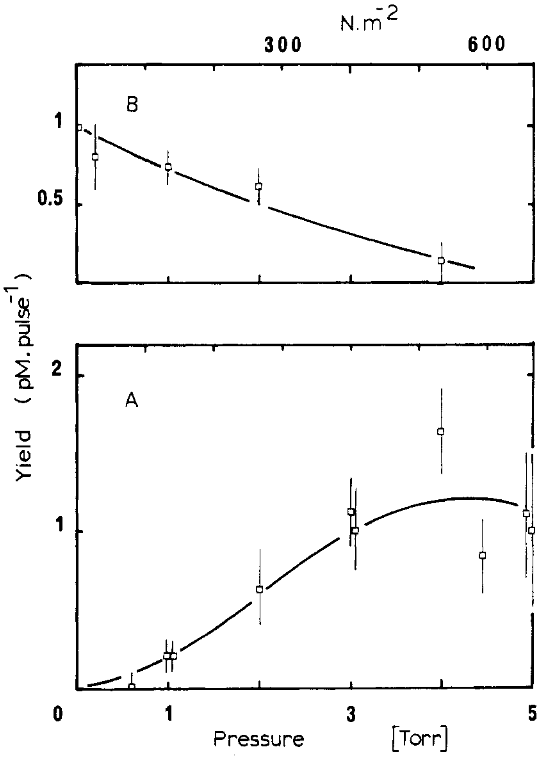

Figure 4. Yield of 1-pentene in the IRMP reaction of *cis*-2-pentene at a central fluence of about 14 J/cm^2: (A) pressure dependence in pure *cis*-2-pentene; (B) dependence on the pressure of helium added to 2 Torr of *cis*-2-pentene. (Yield relative to that in pure pentene.)

Reaction 1 represents a complex interaction of pentene molecules with the radiation field of the laser beam, together with collisional exchange of energy between molecules such as has been modeled, for example, by Starov et al.[16] The *cis*-2-C$_5$H$_{10}$‡ formed in reaction 1 will have a broad distribution of vibrational energies determined by the radiation flux and fluence and by the pressure; this is increasingly truncated above the reaction threshold energy

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TABLE II: Rates and Probabilities of Dissociation and Product Ratios in the IRMP Decomposition of *cis*-2-Pentene

expt	*p*, Torr	fluence, J/cm^2	*R*(CH$'_3$), pmol/pulse	$P^a \times 10^3$	1-C_4H_8 + C_3H_6/C_4H_6	C_3H_6/1-C_4H_8	C_2H_4/C_3H_6
27	1.00	14	63.9	5.86	0.583	0.768	
29	1.00	14	109.3	10.03	0.588	0.756	0.353
30	4.00	14	191.3	4.39	0.531	0.598	0.459
31	0.20	14	11.4	5.23	0.519	0.538	1.0
32	1.97	14	100.0	4.66	0.549	0.654	0.209
33	0.60	14	24.6	3.76	0.579	0.833	0.40
34	5.00	14	152.4	2.80	0.556	0.668	0.50
35	3.00	14	174.0	5.32	0.566	0.707	0.42
46	3.00	14	111.5	3.41	0.499	0.708	0.385
47	1.00	14	40.4	3.71	0.584	0.721	0.321
48	4.40	14	104.2	2.17	0.455	0.715	0.482
54	2.00	19	161.0	7.39	0.511	0.662	0.429
37	4.96	8.4	9.46	0.175	0.619	0.825	0.32
38	1.00	8.4	6.94	0.637	0.667	1.00	0.50
39	2.92	8.4	6.65	0.209	0.581	0.80	0.46
40	0.60	8.4	3.53	0.540	0.697	1.09	0.67
41	0.20	8.4	1.58	0.725	0.857	1.4	
43	4.00	8.4	5.32	0.122	0.596	0.806	0.41
45	2.00	8.4	3.71	0.170	0.619	0.857	0.50

[a] *P* is the probability of dissociation per pulse for a molecule in the central cylindrical portion of the focused beam; see text.

by the removal of the most energetic molecules via reaction 2; this distribution will vary rapidly with time during and after the laser pulse. Reaction 3 in the vacuum UV photolysis is thought to involve methylallyl radicals carrying excess vibrational energy from the original excitation of 2-pentene. This seems rather less likely in the present system, in which the dissociating molecules will tend to have much less energy in excess of the dissociation threshold than with vacuum UV excitation. Nevertheless, 1,3-butadiene is a major product and must almost certainly be formed in reaction 3; this will be discussed further below.

Given the occurrence of reaction 3, the reaction of hydrogen atoms formed therein must be added, together with subsequent radical reactions

$$H + 2\text{-}C_5H_{10} \rightarrow C_2H_5CHC_2H_5^{\ddagger} \qquad (7a)$$

$$\Delta H = -159 \text{ kJ mol}^{-1}$$

$$\rightarrow CH_3CHCH_2C_2H_5^{\ddagger} \qquad (7b)$$

$$C_2H_5CHC_2H_5^{\ddagger} \rightarrow 1\text{-}C_4H_8 + CH_3 \qquad (8)$$

$$\Delta H = +105 \text{ kJ mol}^{-1}$$

$$CH_3CHCH_2C_2H_5^{\ddagger} \rightarrow C_3H_6 + C_2H_5 \qquad (9)$$

$$M + C_5H_{11}^{\ddagger} \rightarrow M + C_5H_{11} \qquad (10)$$

$$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4 \qquad (11a)$$

$$\rightarrow C_3H_8 \qquad (11b)$$

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad (12a)$$

$$\rightarrow n\text{-}C_4H_{10} \qquad (12b)$$

$$C_2H_5 + CH_3CHCHCH_2 \rightarrow \text{products} \qquad (13)$$

The free-radical origin of the majority of the products was confirmed by the effect of added oxygen. Even 10% O_2, however, failed to suppress product formation completely, probably because the high concentration of radicals formed in the pulsed, focused laser beam would require a very high concentration of radical scavenger to compete with radical–radical processes.

From the proposed mechanism, the yield of the primary dissociation, reaction 2, may be evaluated from a summation of products formed from the CH_3 radical. Corrections were made for the branching ratio in reactions 5 and 11, taking values from the literature[22] for this and other calculations

$$R(CH_3) = 2R(4) + R(5) + R(11) =$$
$$2R(C_2H_6) + 3.02R(CH_2{=}CHCH(CH_3)_2) + 1.036R(C_3H_8)$$

Methyl radicals are also formed, however, together with 1-C_4H_8, in the secondary reaction, 8, so that the primary yield of methyl radicals becomes

$$R(CH_3') = R(CH_3) - R(1\text{-}C_4H_8)$$

Values of $R(CH_3')$ are shown in Table II.

While the products found in the present study are similar to those from the vacuum UV photolysis and the mechanism appears similar, there are important quantitative differences. The effects of pressure are notably different in the two systems. In the vacuum UV photolysis, increasing pressure simply leads to increasing collisional quenching of vibrationally excited species, in particular the $CH_3CHCHCH_2$ and C_5H_{11} radicals formed in reactions 2 and 7, respectively. In the IRMP decomposition, the effect of pressure is much more complex, affecting both the absorption process and the subsequent decomposition reactions during and after the laser pulse. With the weakly focused laser beam employed, because the decomposition has a strong dependence on fluence, the reaction can to a good approximation be assumed to occur almost entirely in the central, roughly cylindrical section of the irradiated gas, which in our present system can be estimated to be 0.16 cm in diameter and 10 cm long, with a volume of 0.2 cm^3. With a fluence of 10 J/cm^2, for example, a temperature rise of about 800 K within the central zone can be estimated, using our absorption measurements and known values of C_p for *cis*-2-pentene, assuming no heat loss during the pulse. This temperature rise should be approximately independent of pressure; what does depend very much on pressure, however, is the nature of the decomposition at the molecular level. At the lowest pressure used, 0.2 Torr, the mean free path is about equal to the radius of the reaction zone, so that after excitation molecules will diffuse quickly into the surrounding cold gas, and the high temperature of the reaction zone will be quickly dissipated. There will be little thermal reaction following the pulse, and the observed decomposition will be largely that of isolated vibrationally excited molecules, occurring in competition with collisional deactivation. At 5 Torr, on the other hand, the highest pressure used, the mean free path is about 4% of the radius of the reaction zone. Molecules excited in the pulse, and radical intermediates, will remain in a high-temperature gas for some time before cooling by conduction can occur. Thus, in going from 0.2 to 5 Torr, the system changes from an isolated-molecule decomposition not unlike the vacuum UV photolysis (except that only the ground state is involved), to essentially a bulk thermal decomposition.[23] It is notable that there is no profound change in reaction products in this pressure range or even in product ratios. This indicates that we are dealing with essentially the same chemical mechanism throughout, a unimolecular dissociation followed by a few simple radical reactions with no complex free-radical chain reaction even in the thermal regime; this is to be expected at the relatively high temperature and short reaction times involved.

With the assumption that the decomposition takes place entirely within the central cylindrical portion of the focused beam, as discussed earlier, the probability *P* that a molecule within this zone decomposes in a single pulse can be calculated based on

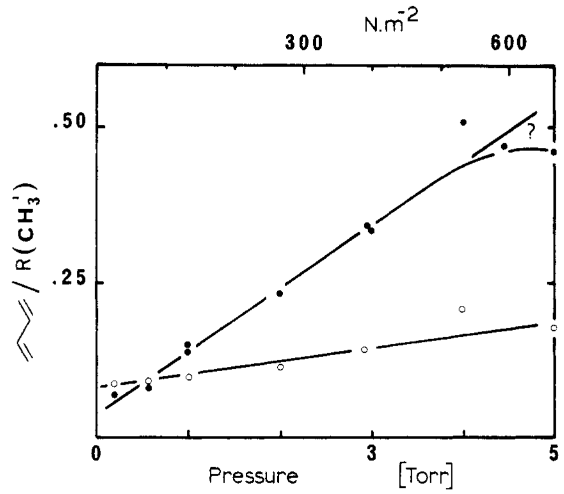


Figure 5. Ratio of the yield of 1,3-butadiene to that of the primary C–CH_3 dissociation as a function of *cis*-2-pentene pressure: (○) fluence of ~8.4 J/cm^2; (●) fluence of 14 J/cm^2.

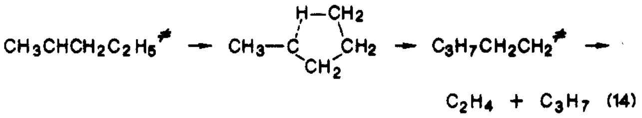
$R(CH_3')$ as a measure of the primary dissociation. Values of P are shown in Table II for two fluences.

These data demonstrate the strong fluence dependence of the decomposition, while the absolute values of P show that the fraction of molecules decomposed in a single pulse was small enough to make secondary reactions of products unlikely. The pressure dependence of P is complicated by attenuation effects; at the higher pressures the fluence is appreciably attenuated by absorption in the 40 cm of pentene (see Figure 1) traversed by the converging beam before reaching the central reaction zone. Combined with the strong dependence on fluence, this effect tends to reduce the observed values of P at higher pressure. When this is taken into account, the probability P appears to be approximately independent of pressure at the higher of the two fluences studies. At the lower fluence, P appears to increase significantly at low pressure. These pressure dependences are complex, involving the relative efficiencies of the "isolated molecule" and "thermal" dissociations and their changing relative importance with pressure, and will not be discussed further.

The variation with pressure in the ratio of reaction 3 to reaction 2 can also be explained in terms of the change in the nature of decomposition. In Figure 5 is shown the ratio of 1,3-butadiene, which should be a measure of reaction 3, to primary methyl radicals formed in reaction 2. This ratio rises markedly with increasing pressure, more so at high fluence than at low. In the vacuum UV photolysis, reaction 3 proceeded via vibrationally excited C_4H_7 radicals formed in the primary dissociation, and their subsequent dissociation *decreased* with increasing pressure as they were deactivated by collision. In the IRMP decomposition the dissociating pentene molecules will tend to have on the average much less energy in excess of the dissociation threshold, and the C_4H_7 radicals will carry away much less vibrational energy. Figure 5 in fact indicates little dissociation of C_4H_7 at low pressure, and the marked increase with rising pressure strongly suggests a *thermal* decomposition of the radical, increasing as thermal reactions in the hot reaction zone become important, as discussed earlier. Direct absorption of laser radiation by the vibrationally excited primary radicals during the rather long pulse may also contribute to their decomposition. The much smaller increase at the lower fluence, where the temperature rise would be much less, is in accord with this explanation.

A somewhat similar explanation can account for the difference in the fragmentation behavior of $C_5H_{11}^{\ddagger}$ radicals (reactions 8 and 9) in the vacuum UV and IRMP systems. In this case the radicals are *chemically* activated in reaction 7 and should possess the same internal energy in both systems. The product ratio (propene + 1-butene)/1,3-butadiene should be a measure of the fraction of C_5H_{11} radicals that decompose. In the vacuum UV photolysis, this fraction falls steadily with increasing pressure, and at 1 Torr about 70% of the radicals should be stabilized.[20] In the present IRMP experiments this ratio remains almost constant at 0.55 ± 0.05 between 0.2 and 5 Torr (Table II). Four separate factors affecting this ratio can be suggested. With increasing pressure, there should be (a) increased collisional deactivation of $C_5H_{11}^{\ddagger}$; (b) an increase in the energy of $C_5H_{11}^{\ddagger}$ as H atoms add to progressively hotter pentene molecules, vibrationally excited either directly in the laser beam or thermally in the hot reaction zone; (c) increased thermal decomposition of stabilized C_5H_{11} radicals in the hot reaction zone following the pulse; (d) increased radical concentrations, favoring combination over decomposition. Factors a and d will tend to decrease the decomposition of $C_5H_{11}^{\ddagger}$ radicals, while b and c will tend to increase it, and the approximately constant fraction observed may correspond to a fortuitous balance between these effects.

Further evidence for thermal decomposition of radicals in the IRMP system is found in the yields of ethylene observed. If ethyl radicals were formed only in reaction 9 and ethylene were formed only by the disproportionation reactions 11a and 12a, the ethylene should be only a small fraction (a few percent) of the propene, which is a measure of reaction 9. In fact, C_2H_4/C_3H_6 varies from about 0.35 to 0.50, (Table II), increasing with increasing pressure, and the ethylene yield is far greater than expected from disproportionation reactions. A probable source of ethylene is the decomposition of ethyl radicals, largely a thermal decomposition, but with perhaps some excess energy carried over from reactions 7b and 9 at lower pressures. An isomerization of $C_5H_{11}^{\ddagger}$ by H-atom transfer through a five-membered ring, followed by decomposition



$$CH_3CHCH_2C_2H_5^{*} \rightarrow CH_3{-}\overset{H-CH_2}{C}\underset{CH_2}{\ \ }CH_2 \rightarrow C_3H_7CH_2CH_2^{*} \rightarrow C_2H_4 + C_3H_7 \quad (14)$$

is perhaps an alternate source of ethylene at low pressure, especially if the $C_5H_{11}^{\ddagger}$ radicals contained extra vibrational energy derived from hot *cis*-2-pentene molecules reacting in reaction 7 as discussed above (factor b). The formation of 1-pentene in the IRMP reaction, apparently as a primary product, shows that a 1,3 sigmatropic transfer of H can occur from the vibrationally excited ground state of *cis*-2-pentene itself, through a four-membered transition state. The probability of this isomerization is small, about 0.5% of the dissociation reaction 2, and approximately independent of pressure. If the activation energy for isomerization were substantially above that for dissociation of 1-pentene, the main fate of newly formed 1-pentene molecules could be dissociation into allyl and ethyl radicals, and the latter could contribute to the high yield of ethylene observed. There is no real evidence for or against this suggestion, which must remain speculative.

Finally, from a general comparison of these results with those of the vacuum UV photolysis, the similarity of the fragmentation processes supports the involvement of the vibrationally excited ground state in the latter. Moreover, it is tempting to add that the formation of 1-pentene in the IRMP decomposition supports the idea that the sigmatropic 1,3 hydrogen shift may also occur through the ground state in the vacuum UV photochemistry. Conversely, the lack of 2-methyl-1-butene formation in the infrared experiments supports the view that the methylene shift proceeds directly through an electronically excited state.

Reactions of 3-Methyl-cis-2-pentene. A mechanism similar to that for *cis*-2-pentene can be proposed to account for the products formed from 3-methyl-*cis*-2-pentene (3McP) shown in Results

$$3McP \underset{}{\overset{nh\nu,\ M}{\rightleftharpoons}} 3McP^{\ddagger} \qquad (15)$$

$$3McP^{\ddagger} \rightarrow CH_3 + CH_2C(CH_3)CHCH_3 \qquad (16)$$

$$\Delta H = 284 \text{ kJ mol}^{-1}$$

$$CH_2C(CH_3)CHCH_3 \rightarrow H + CH_2{=}C(CH_3)CH{=}CH_2 \qquad (17)$$

$$\Delta H = 210 \text{ kJ mol}^{-1}$$

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$$\mathrm{CH_3 + CH_2C(CH_3)CHCH_3 \rightarrow CH_4 + CH_2{=}C(CH_3)CH{=}CH_2} \quad (18a)$$

$$\mathrm{\rightarrow CH_2{=}C(CH_3)CH(CH_3)_2} \quad (18b)$$

$$\mathrm{\rightarrow 3McP,\ 3\text{-}methyl\text{-}}\textit{trans}\mathrm{\text{-}2\text{-}pentene} \quad (18c)$$

$$\mathrm{H + 3McP \rightarrow CH_3CH_2C(CH_3)C_2H_5{}^{\ddagger}} \quad (19)$$

$$\mathrm{CH_3CH_2C(CH_3)C_2H_5{}^{\ddagger} \rightarrow CH_3 + CH_2{=}C(CH_3)C_2H_5,\ etc.} \quad (20)$$

Further steps in the mechanism include stabilization of excited species and radical–radical reactions involving CH_3, C_6H_{13}, and α,β-dimethylallyl radicals. The source of 3,3-dimethyl-1-butene is not obvious. It has been shown recently, however, that excited α,β-dimethylallyl radicals can partly rearrange to the α,α-dimethylallyl structure.[21] The cross combination between the latter and methyl radicals can lead to the formation of 3,3-dimethyl-1-butene and 2-methyl-2-pentene.[21]

As before, the primary split of the β C–C bond in 3-methyl-*cis*-2-pentene may be estimated from the methyl radical yields[24]

$$R(\mathrm{CH_3}') = 2R(\mathrm{C_2H_6}) + 2.81R(\mathrm{CH_2{=}C(CH_3)CH(CH_3)_2} + R(\mathrm{CH_2{=}CHC(CH_3)_3} - R(\mathrm{CH_2{=}C(CH_3)C_2H_5}$$

From the values of $R(\mathrm{CH_3}')$ calculated in this way, the probability P of decomposition per pulse for a molecule in the central cylindrical zone of the focused beam was calculated. Values of $P = 1.95 \times 10^{-3}$ and 4.24×10^{-3} were obtained for fluences of about 12 and 18 J/cm^2, respectively, at a pressure of 4 Torr. These are about half the values obtained with *cis*-2-pentene under comparable conditions, probably reflecting the weaker absorption evident in Figure 1. A more detailed discussion of the decomposition mechanism is not warranted here, but in general the results are similar to those observed in the *cis*-2-pentene system.

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Registry No. 3-Methyl-*cis*-2-pentene, 922-62-3; *cis*-2-pentene, 627-20-3; ethane, 74-84-0; 3-methyl-1-butene, 563-45-1; 1,3-butadiene, 106-99-0; 1-butene, 106-98-9; propene, 115-07-1; propane, 74-98-6; ethylene, 74-85-1; methane, 74-82-8; 2-butene, 107-01-7; *n*-butane, 106-97-8; 2-methyl-1,3-butadiene, 78-79-5; 2-methyl-1-butene, 563-46-2; 2,3-dimethyl-1-butene, 563-78-0; 3,3-dimethyl-1-butene, 558-37-2.

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(22) Values taken were $k_{5a}/k_{5b}/k_{5c} = 0.02/1.0/2.0$ and $k_{6a}/k_{6b} = 0.014$, from ref 17 and $k_{11a}/k_{11b} = 0.036$ and $k_{12a}/k_{12b} = 0.13$, from ref 18.

(23) The effect of added helium in the system is also complex; it will cause collision deactivation at low pressure and limit the temperature rise by dilution at high pressure. It could also slow the cooling process by decreasing the mean free path. The observed effects of helium are compatible with these conclusions.

(24) Taking $k_{18a}/k_{18b}/k_{18c} = 0.1/1.0/1.81$ from ref 17.

Absorption Kinetics of Photochemical Reactions of 2,4,6-Triisopropylbenzophenone and Its Derivatives in Benzene at Room Temperature Studied by Nanosecond Spectroscopy. 2. Laser Chemistry, Molecular Dynamics, Collisions, and Energy Transfer

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Nanosecond laser photolyses of 2,4,6-triisopropylbenzophenones (TIB-X) have been performed in benzene at room temperature, and the characteristic absorption bands due to the highly hindered triplet states are observed around 600~800 nm. For the meta- or para-substituted dicarbonyl TIB-X, the additional bands similar to that of the triplet–triplet absorption of benzophenone or 2-methylbenzophenone are also observed around 450–600 nm. This is interpreted in terms of a rapidly interconverting mixture of two locally excited states in a molecule. It is also presented that triplet TIB-X gives the 1,4-biradicals followed by the formation of the benzocyclobutenols and the dienols.

Introduction

It is well-known that triplet states of *o*-alkylbenzophenones are very short-lived due to the facile intramolecular abstraction of a benzylic hydrogen atom.[1,2] For example, 2-methylbenzophenone undergoes a photochemical intramolecular hydrogen abstraction, yielding the thermally unstable cis- and trans-dienols which decay to the original ketone, and our direct observation of the triplet–triplet ($T' \leftarrow T_1$) absorption indicated that its very short lifetime is due to the facile intramolecular hydrogen abstraction.[2]

In conjunction with the interest in steric effects on the photochemistry of organic compounds, Ito et al.[3] studied the mechanism of photochemical benzocyclobutenol (CB) formation from highly hindered 2,4,6-triisopropylbenzophenones (TIB-X): The primary process of the reaction was thought to be the triplet ketone (T_1) formation followed by the triplet 1,4-biradical (^{3}BR) for-

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